

# Synthesis and Crystal Structure of the New Ternary Halide Series $\text{Ba}_2\text{MCl}_7$ (M = Gd–Yb, Y) Containing the Highly Efficient Up-Conversion Material $\text{Ba}_2\text{ErCl}_7$

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Received June 4, 1996. Revised Manuscript Received August 9, 1996<sup>®</sup>

Single crystals of the compounds  $\text{Ba}_2\text{MCl}_7$  (M = Gd–Yb, Y) can be grown from stoichiometric melts of the binary chlorides using the Bridgman technique. The crystal structure of  $\text{Ba}_2\text{ErCl}_7$  and  $\text{Ba}_2\text{GdCl}_7$  was determined by direct and Fourier methods using single crystal X-ray diffraction data [ $\text{Ba}_2\text{ErCl}_7$ : monoclinic, space group  $P2_1/c$ ,  $Z = 4$ ,  $a = 6.794(2)$  Å,  $b = 15.525(2)$  Å,  $c = 10.496(2)$  Å,  $\beta = 90.54(2)^\circ$ , 3216 reflections,  $R = 0.034$ ;  $\text{Ba}_2\text{GdCl}_7$ : monoclinic,  $P2_1/c$ ,  $Z = 4$ ,  $a = 6.826(1)$  Å,  $b = 15.584(2)$  Å,  $c = 10.557(1)$  Å,  $\beta = 90.67(1)^\circ$ , 3259 reflections,  $R = 0.028$ ]. The compounds  $\text{Ba}_2\text{MCl}_7$  (M = Gd–Yb, Y) are found to be isotopic, their lattice parameters were refined from X-ray powder data. A characteristic feature of the crystal structure is the isolated polyhedron of seven-coordinated  $\text{M}^{3+}$  ions, which may be described as a trigonal prism monocapped on a rectangular prismatic face.  $\text{Ba}_2\text{ErCl}_7$  shows interesting near IR to near UV/vis up-conversion properties.

## Introduction

Ternary halides of the lanthanide elements and in particular of erbium have attracted attention as IR to VIS up-conversion materials.<sup>1,2</sup> Due to their high stability against air and moisture, the fluorides are the most investigated compounds among the halides. On the other hand, the heavier halides are attractive because of their lower phonon energies and the resulting reduction in multiphonon relaxation rates.<sup>2</sup> The latter, however, are generally very moisture-sensitive compounds, and they could be examined only under special precautions. For up-conversion laser applications the chloride crystals should thus fulfill both requirements, high efficiency and enough stability against moisture.

In an attempt to find new moisture-stable up-conversion compounds, we investigated the systems  $\text{BaCl}_2/\text{MCl}_3$  (M = Ce–Lu, La, Y). Existing phase diagrams indicate the formation of  $\text{Ba}_2\text{MCl}_7$  type compounds for M = La,<sup>3a</sup> Sm,<sup>3a</sup> Gd,<sup>3a</sup> Yb,<sup>3a</sup> Y.<sup>3b</sup> A determination of their crystal structure has not been performed until recently, when a Japanese industrial research group mentioned the compound  $\text{Ba}_2\text{ErCl}_7$  in a patent application, however, without giving detailed information on the structure refinement or a discussion on the crystal structure.<sup>4</sup> In a more systematical approach we have

now synthesized a series of  $\text{Ba}_2\text{MCl}_7$  type compounds. We found them to exist with M = Gd–Yb, Y and determined their crystal structure for the examples of  $\text{Ba}_2\text{ErCl}_7$  and  $\text{Ba}_2\text{GdCl}_7$ . The structural features of this new structure type will be discussed in the following, the spectroscopic properties will be mentioned only briefly here, details are given elsewhere.<sup>5</sup>

## Experimental Section

The lanthanide chlorides  $\text{MCl}_3$  were prepared from the respective oxides (Johnson Matthey, 99.999%) following the ammonium halide route.<sup>6</sup>  $\text{BaCl}_2$  was obtained from  $\text{BaCO}_3$  (Merck, 99.99%) by dissolving it in concentrated HCl and evaporating the remaining solution to dryness. All chlorides were sublimed in tantalum tubes under high vacuum ( $10^{-5}$  mbar) for purification.

Small crystals of the compounds  $\text{Ba}_2\text{MCl}_7$  (M = Gd–Yb, Y) were obtained from melts of stoichiometric mixtures of the binary chlorides in silica tubes using the Bridgman technique. An analogous procedure to obtain the compounds with M = Ce–Eu, La, Lu, Sc failed.

For X-ray investigations small transparent crystals ( $0.1 \times 0.15 \times 0.15$  mm) of pink  $\text{Ba}_2\text{ErCl}_7$  and colorless  $\text{Ba}_2\text{GdCl}_7$  were selected under inert-gas conditions in a glovebox using a microscope equipped with polarisator/analysator and sealed in thin-walled glass capillaries (i.d. = 0.1 mm). The quality of the crystals was checked by X-ray oscillation and Weissenberg techniques. X-ray intensities of high-quality crystals were measured with a four-circle diffractometer (Enraf Nonius CAD 4); collection parameters are given in Table 1.

The systematic absences observed in the collected data set and the X-ray photographs led to the space group  $P2_1/c$  (No. 14). Solution and refinement of the structure were successfully done using the programs SHELXS86 and SHELXL93,<sup>7</sup> respectively, after Lorentz and absorption corrections had been

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<sup>®</sup> Abstract published in *Advance ACS Abstracts*, October 1, 1996.

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**Table 1. Crystal Data for  $\text{Ba}_2\text{ErCl}_7$  (I) and  $\text{Ba}_2\text{GdCl}_7$  (II)**

	I	II
lattice parameters [ $\text{\AA}$ , deg]	$a = 6.794(2)$ $b = 15.525(2)$ $c = 10.496(2)$ $\beta = 90.54(2)$ 1107.04(1)	$a = 6.826(1)$ $b = 15.584(2)$ $c = 10.557(1)$ $\beta = 90.67(1)$ 1122.31(1)
volume [ $\text{\AA}^3$ ]	4	
no. of formula units, $Z$		monoclinic
crystal system		$P2_1/c$ (No. 14)
space group		Mo $\text{K}\alpha$ (graphite monochromator)
radiation		20
temp [°C]		$2^\circ < 2\theta < 70^\circ$
data range		empirical, $\psi$ scans for six reflections
absorption correction		
extinction coefficient	0.0034(1)	0.0052(2)
$\mu$ [ $\text{cm}^{-1}$ ]	161.7	143.7
no. of collected reflections	5883	3983
no. of unique reflections	3216	3259
no. of reflections with ( $I > 2\sigma$ )	2815	2924
$R_{\text{int}}$	0.0364	0.0207
goodness of fit	1.17	1.05
$R1$ (all data); $wR2$	0.0341; 0.0696	0.0284; 0.0715
$R1$ ; $wR2$ ( $I > 4\sigma$ )	0.0256; 0.0634	0.0226; 0.0690

**Table 2. Positional Parameters and Equivalent Isotropic Displacement Parameters for  $\text{Ba}_2\text{ErCl}_7$  and  $\text{Ba}_2\text{GdCl}_7$  (in Italics)**

	$x/a$	$y/b$	$z/c$	$10^3 U_{\text{eq}}$ [ $\text{\AA}^2$ ] <sup>a</sup>
Er	0.21702(4)	0.62693(2)	0.21801(3)	9.80(9)
<i>Gd</i>	0.21802(3)	0.62687(1)	0.21671(2)	12.03(8)
Ba1	0.73647(6)	0.77984(3)	0.45076(4)	13.81(10)
	0.73692(4)	0.77938(2)	0.44920(3)	16.15(9)
Ba2	0.26439(6)	0.56095(3)	0.67645(4)	13.96(10)
	0.26439(4)	0.56141(2)	0.67572(3)	16.26(9)
Cl1	0.9992(2)	0.6044(1)	0.4294(1)	14.8(3)
	0.9973(1)	0.60391(9)	0.4299(1)	17.3(2)
Cl2	0.4891(2)	0.7573(1)	0.1980(1)	13.1(2)
	0.4914(1)	0.75818(8)	0.1958(1)	15.2(2)
Cl3	0.0006(2)	0.7724(1)	0.2053(1)	15.3(3)
	0.9977(1)	0.77362(8)	0.2032(1)	17.2(2)
Cl4	0.4874(2)	0.6049(1)	0.4144(1)	14.1(2)
	0.4895(1)	0.60450(8)	0.4159(1)	16.9(2)
Cl5	0.2932(3)	0.4595(1)	0.2132(2)	28.8(4)
	0.2955(2)	0.45774(9)	0.2116(1)	32.5(3)
Cl6	0.8693(2)	0.5705(1)	0.1236(1)	18.6(3)
	0.8624(2)	0.57037(9)	0.1232(1)	21.7(2)
Cl7	0.2896(3)	0.6398(1)	0.9710(1)	32.3(5)
	0.2840(2)	0.6427(1)	0.9657(1)	36.7(4)

$$^a U_{\text{eq}} = 1/3[U_{33} + 1/\sin^2 \beta(U_{11} + U_{33} + 2U_{13} \cos \beta)].^{12}$$

applied to all data. The results of the structure refinement are given in Tables 2 and 3.

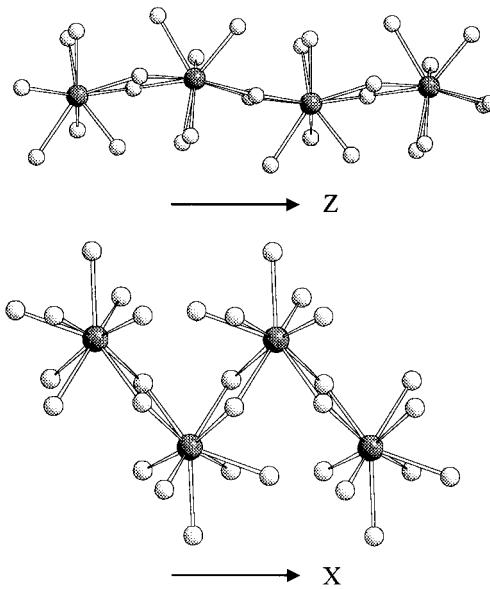
Powder samples of all compounds were analyzed by X-ray powder diffraction using a Guinier-Simon camera (Enraf Nonius). The measured reflection positions were corrected with respect to an internal standard ( $\text{SiO}_2$ ) and lattice parameters were refined based on the single-crystal structure determination by least-squares procedures (program SOS1 and SOS2<sup>8</sup>). The data are given in Table 4.

Up-conversion luminescence spectra of  $\text{Ba}_2\text{ErCl}_7$  were recorded at 20 K after excitation by a Ti sapphire laser at 974.6 nm.

## Results and Discussion

Small single crystals of  $\text{Ba}_2\text{MCl}_7$  ( $\text{M} = \text{Gd} - \text{Yb}$ ,  $\text{Y}$ ) for X-ray diffraction are obtained from melts of stoichiometric mixtures of the respective binary halides. However, due to the incongruent melting of these compounds, bulk single-crystal growth has to start with an

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**Figure 1.** Chains of edge-connected  $[\text{Ba}(1)\text{Cl}_9]$  polyhedra (a, top) and  $[\text{Ba}(2)\text{Cl}_9]$  polyhedra (b, bottom) running along the  $c$  and the  $a$  axes, respectively; dark spheres =  $\text{Ba}^{2+}$ , shadowed spheres =  $\text{Cl}^-$ .

off-stoichiometric mixture of the binary chlorides, with an excess on the lanthanide chloride side.

Single-crystalline materials are relatively stable to moisture when compared to binary or ternary lanthanide chlorides such as  $\text{ErCl}_3$ ,  $\text{GdCl}_3$ ,  $\text{Cs}_3\text{Er}_2\text{Cl}_9$ ,  $\text{RbGd}_2\text{Cl}_7$ , or  $\text{NaErCl}_4$ . After several days, however, the crystal faces turned cloudy when exposed to air. These are important properties with respect to the laser potential of  $\text{Ba}_2\text{ErCl}_7$  and corresponding erbium-doped host lattices.

All compounds are isotropic, and their structure can be described in the monoclinic space group  $P2_1/c$ . The crystal parameters are given in Tables 1 and 2 for  $\text{Ba}_2\text{ErCl}_7$  and  $\text{Ba}_2\text{GdCl}_7$ , respectively. Lattice parameters are summarized in Table 4 for the whole series of synthesized compounds.

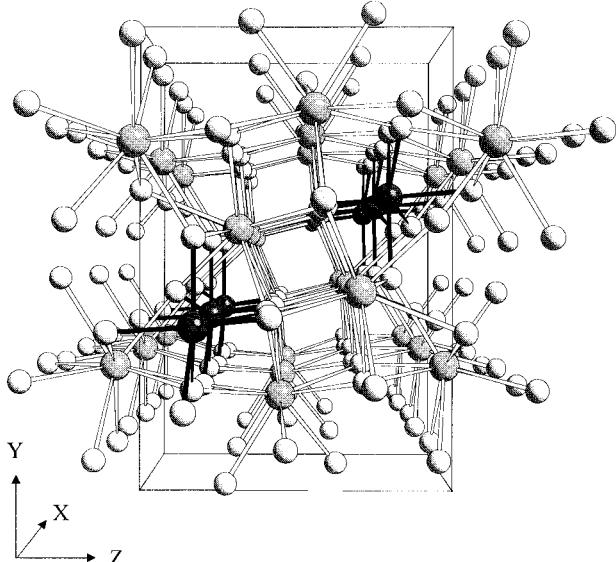
The structural features shall now be described for  $\text{Ba}_2\text{ErCl}_7$ : Two crystallographically different  $\text{Ba}^{2+}$  ions,  $\text{Ba}(1)^{2+}$  and  $\text{Ba}(2)^{2+}$ , are present in the structure, each of them being 9-fold coordinated with typical  $\text{Ba}-\text{Cl}$  distances ranging from 3.08 to 3.33  $\text{\AA}$  (Table 3). The  $[\text{Ba}(1)\text{Cl}_9]$  polyhedra are linked via opposite edges to form chains according to  $[\text{Ba}(1)\text{Cl}_{4/2}\text{Cl}_5]$  running along the  $c$  axis (Figure 1a). The  $[\text{Ba}(2)\text{Cl}_9]$  polyhedra build up zig-zag chains along the  $a$  axis (Figure 1b). A three-dimensional network is built by connecting these chains via common triangular faces. The  $\text{Er}^{3+}$  ions are incorporated into this network (Figure 2), building  $[\text{ErCl}_7]$  polyhedra in the form of trigonal prisms, capped on one rectangular face. The polyhedra are slightly distorted ( $C_1$  symmetry, see also Table 3 and Figure 3) and isolated from each other leading to the extremely long nearest-neighbor  $\text{Er}^{3+}-\text{Er}^{3+}$  distance of 6.48  $\text{\AA}$ . The  $\text{Er}-\text{Cl}$  distances within the  $[\text{ErCl}_7]$  polyhedra (Table 3) range from 2.65 to 2.77  $\text{\AA}$  and correspond very well to the expected values. They are, according to the  $\text{Er}^{3+}$  site symmetry, all slightly different. Although mono-capped trigonal prisms are not known as coordination polyhedra in the crystal chemistry of binary lanthanide chlorides, they occur in several ternary halides like

**Table 3. Selected Internuclear Distances [Å] for  $\text{Ba}_2\text{ErCl}_7$  and  $\text{Ba}_2\text{GdCl}_7$  (in Italics)**

Er—Cl1	2.702(2)	Ba1—Cl1	3.265(2)	Ba2—Cl1	3.215(2)/3.316(2)
<i>Gd—</i>	<i>2.747(1)</i>		<i>3.269(1)</i>		<i>3.222(1)/3.321(1)</i>
—Cl2	2.751(2)	—Cl2	3.146(2)/3.158(1)	—Cl2	3.215(2)
	2.780(1)		<i>3.157(1)/3.169(1)</i>		<i>3.216(1)</i>
—Cl3	2.698(2)	—Cl3	3.156(2)/3.306(2)	—Cl3	3.162(2)
	2.740(1)		<i>3.167(1)/3.307(1)</i>		<i>3.165(1)</i>
—Cl4	2.770(2)	—Cl4	3.221(2)	—Cl4	3.227(2)/3.225(1)
	2.809(1)		<i>3.223(1)</i>		<i>3.230(2)/3.237(1)</i>
—Cl5	2.650(2)	—Cl5	3.283(2)	—Cl5	3.226(2)
	2.689(1)		<i>3.264(1)</i>		<i>3.231(2)</i>
—Cl6	2.699(2)	—Cl6	3.078(2)	—Cl6	3.071(2)
	2.754(1)		<i>3.092(1)</i>		<i>3.085(1)</i>
—Cl7	2.651(2)	—Cl7	3.290(2)	—Cl7	3.329(2)
	2.704(1)		3.327(2)		3.316(1)

**Table 4. Lattice Parameters of  $\text{Ba}_2\text{MCl}_7$  Type Compounds ( $P2_1/c$ ,  $Z = 4$ )**

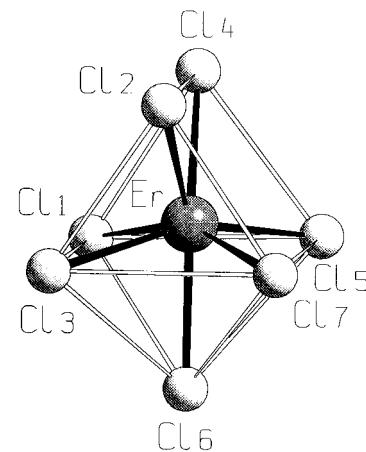
M	$a$ [Å]	$b$ [Å]	$c$ [Å]	$\beta$ [deg]
Gd	6.819(2)	15.578(3)	10.551(2)	90.66(1)
Tb	6.810(2)	15.553(3)	10.536(2)	90.61(2)
Dy	6.801(3)	15.540(4)	10.517(3)	90.56(3)
Ho	6.796(1)	15.521(2)	10.491(1)	90.54(1)
Er	6.792(1)	15.514(2)	10.489(1)	90.50(1)
Y	6.794(2)	15.528(3)	10.500(2)	90.49(2)
Tm	6.779(2)	15.501(2)	10.483(2)	90.43(2)
Yb	6.764(1)	15.484(2)	10.465(1)	90.41(1)



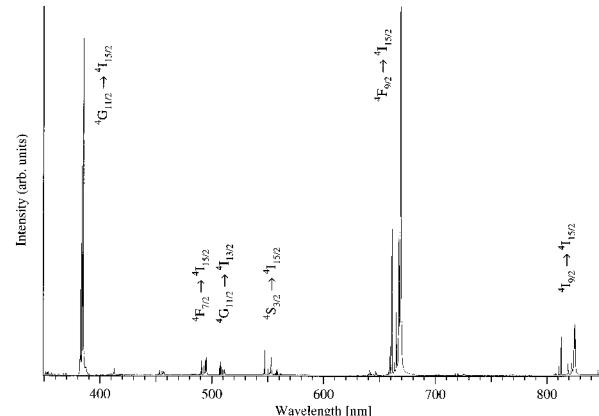
**Figure 2.** Crystal structure of  $\text{Ba}_2\text{ErCl}_7$ : perspective view along the  $a$  axis; dark spheres =  $\text{Er}^{3+}$ ; gray spheres =  $\text{Ba}^{2+}$ ; small shadowed spheres =  $\text{Cl}^-$ ; the  $\text{Er}-\text{Cl}$  bonds are emphasized.

$\text{Na}_2\text{EuCl}_5$ <sup>9</sup> or  $\text{KDy}_2\text{Cl}_7$ .<sup>10</sup> Here, the polyhedra are always linked, and hence the  $\text{Ba}_2\text{MCl}_7$  type chlorides are the first examples with isolated  $[\text{MCl}_7]$  units.

Within the lanthanide series, the existence of  $\text{Ba}_2\text{MCl}_7$  type compounds is shown for  $\text{M} = \text{Gd—Yb}$ . With increasing size of the trivalent ion the 7-fold coordination obviously cannot be retained without structural changes. Another structure type occurs for  $\text{M} = \text{La, Ce—Pr}$  which can be seen as a three-dimensional fluorite type superstructure<sup>11a</sup> and has, due to a certain phase width, approximately the composition  $\text{Ba}_5\text{M}_2\text{Cl}_{16}$ .<sup>11b</sup> This is, according to  $\text{Ba}_5\text{M}_2\text{Cl}_{16} = \text{Ba}_{2.19}\text{M}_{0.88}\text{Cl}_7$ , very



**Figure 3.** Coordination polyhedron of  $\text{Er}^{3+}$  in  $\text{Ba}_2\text{ErCl}_7$ ; the cap over one rectangular face of the trigonal prism is pointing downward.



**Figure 4.** Up-conversion luminescence spectrum of  $\text{Ba}_2\text{ErCl}_7$  at 20 K at excitation of the  $4\text{I}_{15/2}$  to  $4\text{I}_{11/2}$  transition at 974.6 nm.

close to  $\text{Ba}_2\text{MCl}_7$  and might be the reason that the respective phase diagrams indicate the formation of the latter. With the smaller  $\text{Lu}^{3+}$  ion, a new structure type seems to occur, which has not been determined up to now.

$\text{Ba}_2\text{ErCl}_7$  and solid solutions of  $\text{Ba}_2\text{Y}_{1-x}\text{Er}_x\text{Cl}_7$  show promising near-IR to near-UV and vis up-conversion luminescence properties. Upon excitation at either 803 or 980 nm, an intense yellowish green ( $\sim 550$  nm) transition from  $4\text{S}_{3/2}$  to  $4\text{I}_{15/2}$  and an unusually strong  $4\text{G}_{11/2}$  to  $4\text{I}_{15/2}$  (385–390 nm) luminescence is observed. When compared to other known up-conversion materials based on ternary erbium fluorides or chlorides, a semi-quantitative analysis<sup>5a</sup> revealed that  $\text{Ba}_2\text{ErCl}_7$  is one of the most efficient up-conversion chlorides at present,

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especially if the intensities of several emission multiplets ranging from the green to the near-UV are taken into account. At low temperatures (20 K) after excitation at 974.6 nm the up-conversion luminescence spectrum is dominated by red ( $^4F_{9/2}$  to  $^4I_{15/2}$ , 665 nm) and near-UV ( $^4G_{11/2}$  to  $^4I_{15/2}$ , 385 nm) transitions (Figure 4).

### Conclusions

The systematic search for new host lattices in the systems  $\text{BaCl}_2/\text{MCl}_3$  ( $\text{M} = \text{Ce-Lu, Y, La}$ ) has produced relatively air-stable host materials which are of interest for up-conversion laser investigations. Complete air- and moisture-stable lanthanide chlorides, however, are hard to obtain. This is due to the pronounced affinity of the lanthanide ions to oxygen containing ligands such as  $\text{H}_2\text{O}$ . We are currently investigating potential

host lattices such as  $\text{Cs}_3\text{Tl}_2\text{Cl}_9$  and  $\text{Cs}_2\text{TlCl}_5$ ,<sup>5a</sup> which are known to be air-stable compounds.

**Acknowledgment.** We are indebted to Th. Armbruster for the use of a four-circle diffractometer. This work was financially supported by the Swiss National Science Foundation (20-43'116.95) and the priority program Optics II of the Swiss Board of Federal Institutes of Technology (project no. 232).

**Supporting Information Available:** Tables of crystal data and structure refinement, atomic coordinates and equivalent displacement parameters, bond lengths and angles as well as anisotropic displacement parameters are available for both compounds (14 pages). Ordering information is given on any current masthead page.

CM960324F